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| (54) Title: NICKEL DIIMINE CATALYSTS WITH METHYLALUMOXANE AS COCATALYST, METHOD OF POLYMERIZATION OF OLEFINS THEREWITH AND POLYMERS PRODUCED | | |
| (57) Abstract Tetrasubstituted diphenyl diimine nickel complexes further comprising e.g. ACAC ligands and their fluorinated analogs as additional ligands are used in conjunction with methylalumoxane and a support to polymerize alpha olefins or copolymerize plural alpha olefins in the slurry phase. | | |

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NICKEL DIIMINE CATALYSTS WITH METHYLALUMOXANE AS COCATALYST, METHOD OF POLYMERIZATION OF OLEFINS THEREWITH AND POLYMERS PRODUCED

BACKGROUND

This invention relates to homopolymerization of mono-1-olefin monomers, such as ethylene and propylene, and copolymerization of a mono-1-olefin monomers, such as ethylene and propylene, with at least one higher alpha-olefin comonomer.

It is well known that mono-1-olefins, such as ethylene and propylene, can be polymerized with catalyst systems employing transition metals such as titanium, vanadium, chromium, nickel and/or other metals, either unsupported or on a support such as alumina, silica, titania, and other refractory metals. Supported polymerization catalyst systems frequently are used with a cocatalyst, such as alkyl boron and/or alkyl aluminum compounds. Organometallic catalyst systems, i.e., Ziegler-Natta-type catalyst systems usually are unsupported and frequently are used with a cocatalyst, such as methylaluminoxane.

It is also well-known that, while no polymer production process is easy, slurry, or loop, polymerization processes are relatively much more commercially desirable than other polymerization processes. Furthermore, the type of polymerization process used can have an effect on the resultant polymer. For example, higher reactor temperatures can result in low catalyst activity and productivity, as well as a lower molecular weight polymer product. Higher reactor pressures also can decrease the amount of desirable branching in the resultant polymer.

Most polymer products made in slurry processes, especially those polymer products made using supported chromium catalyst systems, have a broader molecular weight distribution and, therefore, the polymer product is much easier to process into a final product. Polymers made by other processes, such as, for example, higher temperature and/or higher pressure solution processes, can produce polymers having a narrow molecular weight distribution; these polymers can be much more difficult to process into an article of manufacture.

Unfortunately, many homogeneous organometallic catalyst systems have low activity, high consumption of very costly cocatalysts, like methylaluminoxane (MAO), and can produce low molecular weight polymers with a

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narrow molecular weight distribution. Furthermore, even though MAO can be necessary to produce a polymer with desired characteristics, an excess of MAO can result in decreased catalyst system activity. Additionally, these types of homogeneous catalyst systems preferably are used only in solution or gas phase polymerization processes.

SUMMARY OF THE INVENTION

The present invention provides novel catalyst systems useful for polymerization, for example, catalyst systems which are relatively simple to make, have increased activity and increased productivity.

The invention also provides catalyst systems which have reduced cocatalyst consumption, and/or which provide an improved polymerization process.

The invention further provides homopolymers of mono-1-olefins and copolymers of at least two different mono-1-olefin(s) that can be processed easily, as indicated by increased branching and a broad molecular weight distribution, and/or which have an increased molecular weight.

In accordance with this invention heterogeneous catalyst systems comprising diimine nickel complexes which further comprise additional ligands selected from the group consisting of α -deprotonated- β -diketones, α -deprotonated- β -ketoesters, halogens and mixtures thereof having a formula selected from the group consisting of $\text{Ni}(\text{NCR}'\text{C}_6\text{R}_2\text{H}_3)_2(\text{Y}_2\text{C}_3\text{R}''_2\text{X})_2$ and $\text{Ni}(\text{NCR}'\text{C}_6\text{R}_2\text{H}_3)_2(\text{Y}_2\text{C}_3\text{R}''_2\text{X})\text{Z}$ and methylaluminoxane are provided. Processes to make these catalyst systems also are provided.

In accordance with another embodiment of this invention, slurry polymerization processes comprising contacting ethylene, and optionally one or more higher alpha-olefins, in a reaction zone with heterogeneous catalyst systems comprising diimine nickel complexes which further comprise additional ligands selected from the group consisting of α -deprotonated- β -diketones, α -deprotonated- β -ketoesters, halogens and mixtures thereof in the presence of methylaluminoxane are provided.

In accordance with this invention heterogeneous catalyst systems consisting essentially of diimine nickel complexes which further comprise additional ligands selected from the group consisting of α -deprotonated- β -diketones, α -

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deprotonated- β -ketoesters, halogens and mixtures thereof and methylaluminoxane are provided. Processes to make these catalyst systems also are provided.

In accordance with another embodiment of this invention, slurry polymerization processes consisting essentially of contacting ethylene, and optionally one or more higher α -olefins, in a reaction zone with heterogeneous catalyst systems comprising diimine nickel complexes which further comprise additional ligands selected from the group consisting of α -deprotonated- β -diketones, α -deprotonated- β -ketoesters, halogens and mixtures thereof in the presence of methylaluminoxane are provided.

By use of the term "consisting essentially of" it is intended that the catalyst systems do not contain any further component which would adversely affect the desired properties imparted to the catalyst systems by the components recited after this expression, and that the process of the invention does not contain any further steps which would have an adverse affect on the desired object of the invention.

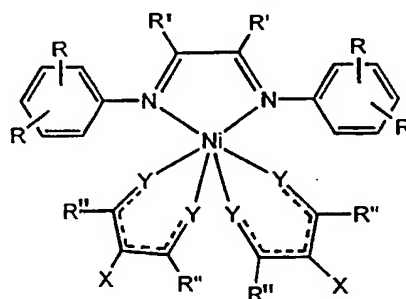
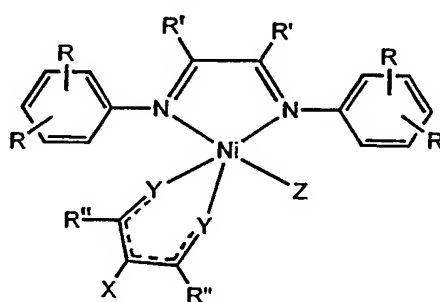
In accordance with yet another embodiment of this invention, compositions comprising homopolymers of ethylene and copolymers of ethylene and one or more higher α -olefins which can be characterized as having high molecular weight, increased branching and a broad molecular weight distribution, are provided.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Catalyst Systems

Catalyst systems of this invention can be characterized as diimine nickel complexes comprising additional ligands selected from the group consisting of β -diketonates, halogens and mixtures thereof having a formula selected from the group consisting of $\text{Ni}(\text{NCR}'\text{C}_6\text{R}_2\text{H}_3)_2(\text{Y}_2\text{C}_3\text{R}''_2\text{X})_2$ and $\text{Ni}(\text{NCR}'\text{C}_6\text{R}_2\text{H}_3)_2(\text{Y}_2\text{C}_3\text{R}''_2\text{X})\text{Z}$ and also represented by general structural formulas as shown below in Compounds I and II,

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Compound ICompound II

wherein R can be the same or different and is selected from the group consisting of branched or linear alkyl or aromatic groups having from about 1 to about 10, preferably from about 1 to about 8, carbon atoms per alkyl group and R can be in any position on the aromatic ring; and

R' can be the same or different and is selected from the group consisting of hydrogen and linear, branched, cyclic, bridging, aromatic, and/or aliphatic hydrocarbons, having from about 1 to about 70, preferably from about 1 to about 20, carbon atoms per radical group.

R substituents on the aromatic rings of the diimine nickel complex can be the same or different, and are selected from the group consisting of branched or linear alkyl (aliphatic) or aromatic groups having from about 1 to about 10, preferably from about 1 to about 8, carbon atoms per alkyl group. Although hydrogen can be used, hydrogen can inhibit synthesis of the ligand. R groups having more than about 8 carbon atoms per group can result in a catalyst system with lower activity and/or productivity. While not wishing to be bound by theory, it is believed that larger substituent groups can cause steric hindrance in the catalyst system, thereby which can decrease catalyst system activity and/or productivity and/or ease of synthesis of the catalyst. Exemplary alkyl substituents are selected from the group

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consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, benzyl, phenyl groups, and mixtures of two or more thereof. Preferably, the R substituent is an electron-donating species, selected from the group consisting of linear or branched aliphatic groups having from about 1 to about 5 carbon atoms per group. Most
5 preferably, the R groups are both the same and are selected from the group consisting of methyl and isopropyl, due to commercial availability and ease of synthesis of the ligand.

The R group can be in any position, i.e., from 2 to 6, on the aromatic ring. Preferably, the R group, which can be the same or different, is either in the 2
10 or 6 position, due to ease of synthesis. Most preferably, for best catalytic activity and productivity, both R groups are the same and are in the 2 and 6 positions on the aromatic ring.

R' substituents can be the same or different and are selected from the group consisting of hydrogen and branched, linear, cyclic, aromatic or aliphatic
15 radicals having from about 1 to about 70 carbon atoms per radical. Further, the R' substituents can be linked, or joined, across the carbon-carbon bridge between the two nitrogen atoms. While not wishing to be bound by theory, it is believed that radicals having more than 70 carbon atoms can add to the steric hindrance of the catalyst systems and hinder catalyst synthesis and/or activity and productivity. Preferably, the
20 R' substituent group is selected from the group consisting of hydrogen and branched, linear, cyclic, aromatic or aliphatic radicals having from about 1 to about 20 carbon atoms per radical, due to commercial availability and ease of synthesis of the ligand. Most preferably, the R' substituent groups are the same or a link across the carbon-carbon bridge between the nitrogen atoms, and the R' substituent is selected from the
25 group consisting of hydrogen and branched, linear, cyclic, aromatic or aliphatic radicals having from about 1 to about 12 carbon atoms per radical, for the reasons given above. Exemplary R' substituents include, but are not limited to, hydrogen, methyl, ethyl, propyl, phenyl, taken together acenaphthyl or cyclobutadienyl. Preferably, the R' substituents are identical and are selected from the group consisting
30 of hydrogen, methyl and acenaphthyl for best resultant catalyst system activity and productivity.

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R"CYCXCYP" substituents, or ligands, on the diimine nickel complex can be the same or different and are selected from the group consisting of α -deprotonated- β -diketones, α -deprotonated- β -ketoesters, halogens and mixtures thereof. The α -deprotonated- β -diketones and α -deprotonated- β -ketoesters can be derived from β -diketone and β -ketoester ligand precursors. Exemplary ligands precursors include, but are not limited to, compounds selected from the group consisting of 2,4-pentanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, allylacetonacetate, benzoylacetonate, benzoyl-1,1,1-trifluoroacetone, 1,1,1-trifluoro-2,4-pentanedione, 1-chloro-1,1-difluoroacetylacetone methyl-4,4,4-trifluoroacetoacetate, 1,1,1-trifluoro-5,5-dimethyl-2,4-pentanedione, ethyl α -methyl-4,4,4-trifluoroacetoacetate, 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione, and 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione.

Preferably, ligand precursors are selected from the group consisting of 2,4-pentanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 1,1,1-trifluoro-2,4-pentanedione, 1-chloro-1,1-difluoroacetylacetone, methyltrifluoroacetoacetate, 1,1,1-trifluoro-5,5-dimethyl-2,4-pentanedione, and ethyl α -methyl-4,4,4-trifluoroacetoacetate. Most preferably, ligands include, but are not limited to 2,4-pentanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 1,1,1-trifluoro-2,4-pentanedione, 1-chloro-1,1-difluoroacetylacetone, and 1,1,1-trifluoro-5,5-dimethyl-2,4-pentanedione for best catalyst system activity as well as best polymer product properties.

R" and X can be the same or different and are selected from the group consisting of hydrogen and linear, branched, cyclic, bridging aromatic and aliphatic hydrocarbon and mixtures of any two or more of these radicals having from about 1 to about 70 carbon atoms per radical group.

The group Z, i.e., halogen, of the diimine nickel complex is selected from the group consisting of fluorine, chlorine, bromine and/or iodine. Preferably, the halogen is selected from the group consisting of chlorine and/or bromine for high catalyst activity and productivity. Most preferably, the halogen is chlorine for best catalyst system activity and productivity.

Y is independently selected from the group consisting of oxygen, sulfur and selenium.

The diimine nickel complex catalyst system disclosed in this application can be prepared by any method known in the art. For example,

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approximate molar equivalents of a diimine ligand and a nickel compound can be contacted in the presence of any compound that can dissolve both the diimine ligand and nickel compound, either partially or completely. The contacting conditions can be any conditions suitable to effect the formation of a diimine nickel complex.

- 5 Preferably, for best product results, the diimine ligand/nickel complex mixture is contacted at room temperature under a dry atmosphere for any amount of time sufficient to form the diimine nickel complex. Completion of the formation of the diimine nickel complex can be evidenced by a color change. Generally, contacting times of about 8, and preferably 12 hours are sufficient. Usually, as a result of the
- 10 preparation procedure, the resultant diimine nickel complex will comprise from about 3 to about 20, preferably from about 5 to about 15, weight percent nickel, based on the total mass of the diimine nickel complex. The presence of oxygen is not thought to be detrimental to this aspect of the preparation procedure.

- In general, diimine ligands are contacted with a nickel β -diketonate or
- 15 nickel β -diketonate halide to form diimine nickel complexes. Typical syntheses of nickel complexes related to those described in this invention can be found in Dieck, H., Svoboda, M., and Greiser, T., Z. Naturforsch B: Anorg. Chem. Organ. Chem., Vol. 36b, pp. 823-832 (1981), herein incorporated by reference. Usually, for ease of catalyst system preparation, the diimine ligand is prepared first. The catalyst
- 20 preparation procedure can vary, depending on the substituents on the diimine ligand. For example, to prepare a specific diimine ligand, wherein R' is hydrogen, a three-component mixture is prepared. A two-fold molar excess of aniline, containing the desired R substituents ($R_nC_6H_{(7-n)}N$, wherein $n = 1,2$), is contacted with a dialdehyde, such as, for example, glyoxal (CHOCHO), in the presence of a compound capable of
- 25 being a solvent for both organic and aqueous compounds. Exemplary solvents for both organic and aqueous compounds include, but are not limited to, methanol, ethanol and/or tetrahydrofuran (THF). The mixture can be contacted, preferably refluxed, under any atmosphere to form the desired ligand. Preferably, the mixture is refluxed for at least 10, preferably 20 minutes, cooled and the desired ligand can be
- 30 recovered. Generally, after refluxing and cooling, the ligand can be recovered in a crystalline form.

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To prepare another specific diimine ligand wherein the R' group is anything other than hydrogen, a similar procedure can be used. For example, at least a two-fold molar excess of aniline or a substituted aniline can be combined with a compound capable of dissolving both organic and aqueous compounds and a very
5 minor amount of formic acid. Then, about a one molar equivalent of an alpha-diketone (R'COCOR') can be added to the mixture. The mixture can be stirred, under atmospheric conditions of temperature and pressure until the reaction is complete and the desired ligand is formed. Preferably, water is absent from the reaction mixture. Generally, the reaction will be complete in about 18, preferably 24
10 hours. A crystalline ligand product can be recovered according to any method known in the art.

The nickel bis(β -diketonate), nickel bis(β -ketoester), nickel β -diketonate halide and nickel β -ketoester halide can be prepared by any method known in the art. Typical syntheses of such nickel complexes can be found in Bullen, G.J.,
15 Mason, R., and Pauling, P., Inorganic Chemistry, Vol. 4, pp. 456-462 (1965), herein incorporated by reference. Alternatively, and especially in the case of nickel β -diketonate halides and nickel β -ketoester halides, the salt of the β -diketone or β -ketoester can be prepared then reacted with the correct quantity of nickel halide. A mixture of an appropriate Brönsted base, such as but not limited to sodium or
20 potassium hydride or sodium or potassium methoxide, is mixed with a solvent capable of dissolving or becoming miscible with the β -diketone or β -ketoester. Exemplary solvents include toluene, benzene, methanol, or ethanol. One molar equivalent of the β -diketone or β -ketoester is added slowly to this mixture. Reaction is known to occur as evidenced by the evolution of heat and a change in the physical
25 appearance of the mixture. Once all reactants have contacted, reaction times from 4 to 12 hours are sufficient to ensure complete reaction. If the product salt of the β -diketone or β -ketoester is not soluble in the solvent chosen, the solvent is removed by filtration or vacuum and the salt dissolved in a solvent in which it is soluble. Exemplary solvents include methanol and ethanol. This solution is then added to a
30 one half molar equivalent of nickel halide that has been suspended or dissolved in the same solvent or a solvent with which the first solvent is miscible. The preceding reactant ratio results in the formation of the nickel bis(β -diketonate) or nickel bis(β -

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ketoester). If the nickel β -diketonate halide or nickel β -ketoester halide are desired, the solution is added to one molar equivalent of nickel halide as described. Reaction is known to occur as evidenced by the formation of a soluble green species. Reaction times of 4 to 12 hours are sufficient to ensure complete reaction. The byproduct sodium or potassium halide salt is then removed from the reaction product by
5 filtration and/or centrifugation. The solvent is removed by vacuum to yield the nickel complex used in the nickel diimine complex synthesis.

After formation of a diimine nickel complex, the diimine nickel complex can be recovered by any method known in the art, such as, for example
10 evaporation and/or vacuum filtration of the solvent. Further, if desired, the diimine nickel complex can be further purified by washing. One exemplary wash compound can be heptane. The diimine nickel complex catalyst system can be recovered and used as a solid, heterogeneous catalyst system.

Reactants, Polymerization and Polymer Products

15 Polymers produced according to the process of this invention can be homopolymers of mono-1-olefins or copolymers of at least two different mono-1-olefins. Exemplary mono-1-olefins useful in the practice of this invention include, but are not limited to mono-1-olefins having from about 2 to about 10 carbon atoms per molecule. Preferred mono-1-olefins include, but are not limited to ethylene,
20 propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 3-methyl-1-butene, 4-methyl-1-pentene, 1-octene, 1-nonene and 1-decene. If the reaction product is a copolymer, one mono-1-olefin monomer can be polymerized with a mono-1-olefin comonomer which is a different alpha-olefin, usually having from about 3 to about 10, preferably from 3 to 8 carbon atoms per molecule. Exemplary comonomers include, but are not
25 limited to, propylene, 1-butene, butadiene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-pentene, and mixtures thereof. Preferably, if the monomer is ethylene, the comonomer is 1-hexene and/or 4-methyl-1-pentene, in order to achieve maximum polymer product toughness. Preferably, if the monomer is propylene, the comonomer is ethylene and/or butadiene in order to achieve maximum polymer product toughness
30 and clarity.

If a comonomer is used, the comonomer can be added to the polymerization reactor, or reaction zone, in an amount within a range of about 1 to

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about 20 weight percent, preferably within 7 to about 18 weight percent, based on the weight of the ethylene monomer. Most preferably, a comonomer is present in the reaction zone within a range of about 10 to about 16 weight percent, in order to produce a polymer having the most desired physical properties.

5 Polymerization of the monomer and optional comonomer must be carried out under slurry, also known as loop/slurry or particle form, polymerization conditions wherein the temperature is kept below the temperature at which polymer swells significantly. Slurry polymerization processes are much easier to operate and maintain than other polymerization processes; a polymer product produced by a slurry
10 process can be recovered much more easily. Such polymerization techniques are well-known in the art and are disclosed, for instance, in Norwood, U.S. Pat. No. 3,248,179, the disclosure of which is hereby incorporated by reference.

The slurry process generally is carried out in an inert diluent (medium), such as, for example, a paraffin, cycloparaffin, and/or aromatic hydro-
15 carbon. Preferably, the inert diluent is an alkane having less than about 12 carbon atoms per molecule, for best reactor operation and polymer product. Exemplary diluents include, but are not limited to propane, n-butane, isobutane, n-pentane, 2-methylbutane (isopentane), and mixtures thereof. Isobutane is the most preferred diluent due to low cost and ease of use.

20 The temperature of the polymerization reactor, or reaction zone, when using isobutane as the reactor diluent, according to this invention, is critical and must be kept within a range of about 5° to about 100°C (41° - 212°F) and preferably within a range of about 10° to about 70°C (50° - 158°F). Most preferably, the reaction zone temperature is within a range of 20° to 60°C (68° - 140°F) for best
25 catalyst activity and productivity. Reaction temperatures below about 10°C can be ineffective for polymerization.

Pressures in the slurry process can vary from about 100 to about 1000 psia (0.76 - 7.6 MPa), preferably from about 200 to about 700 psia. Most preferably, the reaction zone is maintained at a pressure within a range of 300 to 600 psia for
30 best reactor operating parameters and best resultant polymer product. The catalyst system is kept in suspension and is contacted with the monomer and comonomer(s) at sufficient pressure to maintain the medium and at least a portion of the monomer and

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comonomer(s) in the liquid phase. The medium and temperature are thus selected such that the polymer or copolymer is produced as solid particles and is recovered in that form. Catalyst system concentrations in the reactor can be such that the catalyst system content ranges from 0.001 to about 1 weight percent based on the weight of the reactor contents.

The catalyst system and methylaluminoxane (MAO) can be added to the reactor in any order to effect polymerization. For example, catalyst system can be added, then some reactor diluent, such as isobutane, followed by MAO, then more diluent and finally, monomer and optional comonomer. However, as stated earlier, this addition order can be varied, depending on equipment availability and/or desired polymer product properties. Preferably, the catalyst system and MAO are not pre-contacted prior to addition to the polymerization reactor due to a possible decrease in catalyst activity.

The amount of catalyst system and MAO added to the reactor can vary. Generally, a molar excess of MAO is present, relative to the diimine nickel complex. Preferably, the aluminum to nickel (Al:Ni) molar ratio is less than about 1500:1, more preferably within a range of about 50:1 to about 600:1. Most preferably, the molar ratio of aluminum to nickel is within a ratio of 100:1 to 400:1 for best catalyst system activity and productivity.

Two preferred polymerization methods for the slurry process are those employing a loop reactor of the type disclosed in Norwood and those utilizing a plurality of stirred reactors either in series, parallel or combinations thereof wherein the reaction conditions can be the same or different in the different reactors. For instance, in a series of reactors, a chromium catalyst system which has not been subjected to the reduction step can be utilized either before or after the reactor utilizing the catalyst system of this invention.

Polymers produced in accordance with this invention generally have a relatively narrow heterogeneity index (HI), which is a ratio of the weight average molecular weight (M_w) and the number average molecular weight (M_n) (also expressed as M_w/M_n). Polymers produced in accordance with this invention usually have a HI within a range of about 3 to about 10, preferably within a range of about 3 to about 6, for best indication of processability.

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Polymers produced in accordance with this invention are very unique because of a significant amount of short chain branching which can be produced even in the absence of a comonomer added to the reactor. This short chain branching is evidence that some sort of comonomers are produced in-situ in the reactor and are
5 incorporated into the polymer and/or that the catalyst can form short chain branches by rearrangement of the main polymer chain through successive hydride elimination, olefin rotation, and hydride re-addition reactions. This series of steps may not involve discrete intermediates and may rather be a concerted or continuous series of reactions with no distinct intermediates formed. Such rearrangements can be termed
10 "chain walking". Chain walking can be described by the active metal catalyst, i.e. nickel, "walking" a distance along the polymer backbone during polymerization and hence, the short chain branch length can be dictated by the rate of ethylene insertion relative to the combined rates of hydride elimination, olefin rotation, and hydride re-addition. Usually polymers produced in accordance with this invention, wherein no
15 comonomer is added to the polymerization reactor comprise up to about 3000, and generally from about 20 to about 3000 short chain branches per 10,000 (or from about 2 to about 300 short chain branches per 1000) backbone carbon atoms of the polymer. Furthermore, the short chain branches produced comprise both odd and even carbon branches, i.e., branches comprising an odd number of carbon atoms per
20 short chain branch, as well as branches comprising an even number of carbon atoms per short chain branch.

If desired, optional addition of one or more comonomers can be added to the polymerization reactor. The affirmatively added comonomers can further increase the amount of short chain branching in the resultant polymer, or copolymer.
25 Polymers produced with the addition of a comonomer can have a greater number of short chain branches in addition to those generated as described above. If a comonomer is affirmatively added to the polymerization reactor, these polymers usually can comprise up to about 3500, and generally from about 20 to about 3500, short chain branches per 10,000 backbone carbon atoms of polymer.

30 A further understanding of the invention and its advantages is provided by the following examples.

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EXAMPLES

The following Examples illustrate various aspects of the invention. Data are included for each example about polymerization conditions, as well as the resultant polymer. All chemical handling, including reactions, preparation and storage, was performed under a dry, inert atmosphere (usually nitrogen). Unless otherwise indicated, bench scale polymerizations were completed in a 2.6 liter auto-clave reactor at the desired temperature using an isobutane (1.2 liter) slurry. The reactor was heated to 120°C and purged with nitrogen for about 20 minutes. The reactor then was cooled to the desired polymerization temperature and pressurized with isobutane to about 400 psig. A known quantity (mass) of diimine nickel complex catalyst was charged to the reactor against a countercurrent of isobutane and the agitator was set at 490 rpm. If hydrogen was charged to the reactor, hydrogen addition was followed by isobutane. The desired quantity of methylaluminoxane (MAO) (10 weight % in toluene) was charged directly to the reactor via syringe. After the full volume of isobutane was added, ethylene was added to bring the total reactor pressure to 550 psig. Ethylene was fed on demand and the polymerization reaction terminated when ethylene flow into the reactor ceased. Run times for each polymerization reaction are provided in the Tables.

The abbreviations for the catalyst systems used are as follows:

- 20 [(iPr₂Ph)₂DABMe₂]Ni(acac)₂ -
N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(II) bis(acetylacetonate)
- [(iPr₂Ph)₂DABMe₂]Ni(hfacac)₂ -
N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(II) bis(1,1,1,5,5,5-hexafluoroacetylacetonate)
- 25 [(iPr₂Ph)₂DABMe₂]Ni(hfacac)Cl -
N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(II) (1,1,1,5,5,5-hexafluoroacetylacetonate)chloride
- [(iPr₂Ph)₂DABMe₂]Ni(allOacac)₂ -
N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine bis(allylacetylacetonato) nickel(II)
- 30 [(iPr₂Ph)₂DABMe₂]Ni(Phacac)₂ -
N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(II) bis(benzoylacetonate)
- [(iPr₂Ph)₂DABMe₂]Ni(PhCF₃acac)₂ -

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N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(II) bis(benzoyl-1,1,1-trifluoroacetate)



N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(II) bis(1,1,1-

5 trifluoroacetylacetate)



N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(II) bis(1-chloro-1,1-difluoroacetylacetate)



10 N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine bis(methyltrifluoroacetoacetate) nickel(II)



N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(II) bis(1,1,1-trifluoro-5,5-dimethylacetylacetate)

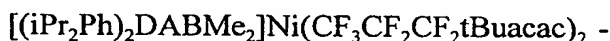
15 $[(iPr_2Ph)_2DABMe_2]Ni(CF_3OEt-\alpha-Meacac)_2 -$

N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine bis(ethyl α -methyl-4,4,4-trifluoroacetoacetate) nickel(II)



N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(II) bis(4,4,4-trifluoro-1-(2-furyl)acetylacetate)

20



N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(II) bis(2,2-dimethyl 6,6,7,7,8,8,8-heptafluoro-3,5-octanedionate)



25 N,N'-bis(2,6-diisopropylphenyl)acenaphthyl nickel(II) bis(hexafluoroacetylacetate)



N,N'-bis(2,6-dimethylphenyl)-2,3-ethylenediimine nickel(II) bis(acetylacetate)



N,N'-bis(2,6-dimethylphenyl)-2,3-butanediimine nickel(II) bis(acetylacetate).

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In general, catalyst systems used for polymerization in the Examples were prepared as described in this application.

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Mass Catalyst (grams) is the mass of catalyst system charged to the polymerization reactor for each Run. Polymer density was determined in grams per cubic centimeter (g/cc) on a compression molded sample, cooled at about 15°C per hour, and conditioned for about 40 hours at room temperature in accordance with ASTM D1505 and ASTM D1928, procedure C. High load melt index (HLMI, g/10 mins) was determined in accordance with ASTM D1238 at 190°C with a 21,600 gram weight. Melt index (MI, g/10 mins) was determined in accordance with ASTM D1238 at 190°C with a 2,160 gram weight. Size exclusion chromatography (SEC) analyses were performed at 140°C on a Waters, model 150 GPC with a refractive index detector. A solution concentration of 0.17 to 0.65 weight percent in 1,2,4-trichlorobenzene was found to give reasonable elution times. Reported weight average molecular weight (M_w) and number average molecular weight (M_n) values (results) need to be multiplied by a factor of 1000 for the actual value. Reported Al:Ni ratio values are expressed as molar ratio values. Values that were not determined are represented as "ND" in the Tables.

EXAMPLE 1

This example shows that high catalyst system productivity can be achieved by substituting one or both of the halide ligands of a diimine nickel dihalide complex with a β -diketonate or β -ketoester ligand.

Polymerizations in the following Runs were carried out as described above, with a reactor pressure of 550 psig ethylene in isobutane slurry at 40°C. MAO was added in a 10% wt/wt solution in toluene. Polymerization results are listed below in Table 1.

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TABLE I

| Run # | Catalyst | Mass cat. (g) | Run Time (mins.) | Productivity (g PE/g Ni) | MI | HLM | Density (g/cc) | Al:Ni |
|-------|---|------------------|------------------------|-----------------------------|----|-----|-------------------|-------|
| 101 | [(iPr ₂ Ph ₂)DABMe ₂]NiBr ₂ | 0.0218 | 13 | 490 | ND | ND | ND | 240 |
| 102 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(CF ₃ CF ₂ CF ₂ CF ₂ Buacac) ₂ | 0.0583 | 4 | 7310 | 0 | 0 | 0.9196 | 150 |
| 103 | [(iPr ₂ Ph ₂)DABMe ₂]NiCl ₂ | 0.0200 | 9 | 11400 | 0 | 0 | 0.9099 | 230 |
| 104 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(hfacac) ₂ | 0.0050 | 4 | 12000 | ND | ND | ND | 1200 |
| 105 | [(iPr ₂ Ph ₂)DABMe ₂]NiCl ₂ | 0.0230 | 30 | 13400 | 0 | 0 | 0.9081 | 200 |
| 106 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(CF ₃ OEt- α -Meacac) ₂ | 0.0163 | 21 | 13900 | 0 | 0 | 0.9074 | 450 |
| 107 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(Phacac) ₂ | 0.0109 | 18 | 17100 | ND | ND | 0.9212 | 610 |
| 108 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(alOacac) ₂ | 0.0209 | 27 | 21300 | 0 | 0 | 0.9157 | 300 |
| 109 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(CF ₃ acac) ₂ | 0.0020 | 8 | 29500 | 0 | 0 | ND | 3300 |
| 110 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(CF ₃ furacac) ₂ | 0.0121 | 17 | 30700 | 0 | 0 | 0.8961 | 610 |
| 111 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(PhCF ₃ acac) ₂ | 0.0165 | 41 | 33700 | 0 | 0 | 0.9137 | 460 |
| 112 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(hfacac) ₂ | 0.0111 | 3 | 35000 | 0 | 0 | 0.8819 | 670 |
| 113 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(CClF ₂ acac) ₂ | 0.0118 | 10 | 96200 | 0 | 0 | 0.8857 | 580 |
| 114 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(hfacac) ₂ | 0.0195 | 15 | 108000 | 0 | 0 | 0.8926 | ND |
| 115 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(tBuCF ₃ acac) ₂ | 0.0114 | 17 | 139000 | ND | ND | 0.8918 | 640 |
| 116 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(CF ₃ acac) ₂ | 0.0041 | 60 | 157000 | 0 | 0 | 0.8955 | 1600 |
| 117 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(hfacac) ₂ | 0.0092 | 18 | 174000 | 0 | 0 | 0.8888 | 810 |

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| Run # | Catalyst | Mass cat. (g) | Run Time (mins.) | Productivity (g PE/g Ni) | MI | HLMI | Density (g/cc) | Al:Ni |
|-------|------------------------------------|------------------|------------------------|-----------------------------|----|------|-------------------|-------|
| 118 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)Cl$ | 0.0062 | 27 | 198000 | 0 | 0 | 0.8871 | 1000 |
| 119 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0052 | 31 | 293000 | 0 | 0 | 0.9100 | 860 |
| 120 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0100 | 31 | 327000 | 0 | 0 | 0.9087 | 750 |
| 121 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0025 | 14 | 378000 | 0 | 0 | 0.9017 | 600 |
| 122 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0040 | 35 | 493000 | 0 | 0 | 0.9111 | 750 |
| 123 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0052 | 31 | 621000 | 0 | 0 | 0.8853 | 1400 |

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The data in Table 1 show that diimine nickel(II) catalyst systems containing β -diketonate or β -ketoester ligands can effectively polymerize ethylene with higher productivity than catalysts containing exclusively diimine and halide ligands (see Runs 101, 103 and 105). The data also show that the addition of a single β -diketonate ligand affords much higher productivity. Also note that reactor temperatures are within commercially acceptable ranges, i.e., between 40 and 80°C.

EXAMPLE 2

This example shows that process conditions can be changed without losing the high productivity attained by one or both of the halide ligands of a diimine nickel dihalide complex with a β -diketonate or β -ketoester ligand. Again, all of the following polymerizations were carried out as described above, with a reactor pressure of 550 psig ethylene in isobutane slurry. MAO was added in a 10% wt/wt solution in toluene. Process conditions were varied by changing the polymerization temperature and, as a result, the quantity of dissolved ethylene in the reaction medium. The structure of the diimine ligand was also varied. Polymerization catalyst systems and results are listed below at temperatures of 27, 60, and 80 °C in Tables 2, 3, and 4, respectively.

TABLE 2 (all Runs were at 27°C)

| Run # | Catalyst | Mass cat. (g) | Run Time (mins) | Productivity (g PE/g Ni) | MI | HLMi | Density (g/cc) | Al:Ni | Mn | Mw | HI |
|-------|--|---------------|-----------------|--------------------------|------|------|----------------|-------|------|------|------|
| 201 | [(iPr ₂ Ph ₂)DABMe ₂]NiBr ₂ | 0.0340 | 15 | 940 | ND | ND | 0.9450 | 160 | ND | ND | ND |
| 202 | [(iPr ₂ Ph ₂)DABAn]NiBr ₂ | 0.0303 | 25 | 1210 | ND | ND | 0.9564 | 200 | ND | ND | ND |
| 203 | [(iPr ₂ Ph ₂)DABMe ₂]NiCl ₂ | 0.0231 | 24 | 1580 | ND | ND | ND | 200 | ND | ND | ND |
| 204 | [(Me ₂ Ph ₂)DABMe ₂]NiBr ₂ | 0.0301 | 17 | 2020 | 0 | 0.05 | 0.9496 | 140 | 239 | 531 | 2.22 |
| 205 | [(Me ₂ Ph ₂)DABH ₂]NiBr ₂ | 0.0294 | 24 | 2510 | 1.4 | 84 | 0.9749 | 140 | 20 | 74 | 3.64 |
| 206 | [(iPr ₂ Ph ₂)DABAn]NiCl ₂ | 0.0343 | 31 | 4080 | 0 | 0 | 0.9421 | 160 | 399 | 1059 | 2.65 |
| 207 | [(Me ₂ Ph ₂)DABH ₂]NiCl ₂ | 0.0233 | 31 | 4950 | 0.46 | 38 | 0.9691 | 140 | ND | ND | ND |
| 208 | [(iPr ₂ Ph ₂)DABMe ₂]NiCl ₂ | 0.0176 | 41 | 26900 | 0 | 0 | 0.9175 | 260 | ND | ND | ND |
| 209 | [(Me ₂ Ph ₂)DABMe ₂]NiCl ₂ | 0.0413 | 60 | 27900 | 0 | 0.07 | 0.9457 | 87 | 95 | 373 | 3.92 |
| 210 | [(Me ₂ Ph ₂)DABH ₂]Ni(acac) ₂ | 0.0362 | 30 | 29000 | 0 | 0.45 | 0.9305 | 120 | ND | ND | ND |
| 211 | [(Me ₂ Ph ₂)DABH ₂]Ni(acac) ₂ | 0.0021 | 9 | 42300 | 0 | 0.07 | 0.9383 | 420 | ND | ND | ND |
| 212 | [(iPr ₂ Ph ₂)DABMe ₂]NiCl ₂ | 0.0309 | 74 | 57700 | 0 | 0 | 0.9132 | 150 | 1038 | 2638 | 2.54 |
| 213 | [(Me ₂ Ph ₂)DABH ₂]Ni(acac) ₂ | 0.0139 | 14 | 78000 | 0 | 0.15 | 0.9180 | 320 | ND | ND | ND |
| 214 | [(Me ₂ Ph ₂)DABMe ₂]Ni(acac) ₂ | 0.0147 | 18 | 78800 | 0 | 0.33 | 0.9331 | 320 | ND | ND | ND |
| 215 | [(Me ₂ Ph ₂)DABMe ₂]Ni(acac) ₂ | 0.0090 | 14 | 82100 | ND | ND | ND | 520 | ND | ND | ND |
| 216 | [(iPr ₂ Ph ₂)DABAn]Ni(hfacac) ₂ | 0.0142 | 25 | 96900 | 0 | 0 | 0.9205 | 580 | 420 | 1425 | 3.4 |

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| Run # | Catalyst | Mass cat. (g) | Run Time (mins) | Productivity (g PE/g Ni) | MI | HLM | Density (g/cc) | Al:Ni | Mn | Mw | HI |
|-------|--|---------------|-----------------|--------------------------|-----|-----|----------------|-------|-----|------|------|
| 217 | $[(\text{Me}_2\text{Ph}_2)\text{DABH}_2]\text{Ni}(\text{hfacac})_2$ | 0.0100 | 9 | 138000 | 5.6 | 215 | 0.9450 | 630 | ND | ND | ND |
| 218 | $[(\text{iPr}_2\text{Ph}_2)\text{DABMe}_2]\text{Ni}(\text{hfacac})_2$ | 0.0204 | 30 | 149000 | 0 | 0 | 0.8951 | 370 | 516 | 1687 | 3.27 |
| 219 | $[(\text{iPr}_2\text{Ph}_2)\text{DABMe}_2]\text{Ni}(\text{hfacac})\text{Cl}$ | 0.0134 | 35 | 199000 | 0 | 0 | 0.9002 | 450 | 360 | 1523 | 4.23 |

TABLE 3 (all Runs were at 60°C)

| Run # | Catalyst | Mass cat. (g) | Run Time (mins) | Productivity (g PE/g Ni) | MI | HLM | Density (g/cc) | Al:Ni | Mn | Mw | HI |
|-------|--|---------------|-----------------|--------------------------|------|------|----------------|-------|-----|------|------|
| 301 | [(Me ₂ Ph ₂)DABH ₂]Ni(acac) ₂ | 0.0161 | 6 | 1580 | ND | ND | ND | 280 | ND | ND | ND |
| 302 | [(Me ₂ Ph ₂)DABH ₂]NiCl ₂ | 0.0229 | 1 | 3810 | 1.7 | 112 | 0.9618 | 150 | 17 | 84 | 4.91 |
| 303 | [(Me ₂ Ph ₂)DABMe ₂]NiCl ₂ | 0.0545 | 16 | 4710 | 0.21 | 22 | 0.9056 | 26 | 33 | 94 | 2.82 |
| 304 | [(Me ₂ Ph ₂)DABH ₂]NiCl ₂ | 0.0274 | 8 | 5130 | 2.5 | 126 | 0.9546 | 73 | 16 | 73 | 4.46 |
| 305 | [(Me ₂ Ph ₂)DABH ₂]NiCl ₂ | 0.0233 | 8 | 5470 | 2.6 | 127 | 0.9530 | 58 | ND | ND | ND |
| 306 | [(iPr ₂ Ph ₂)DABAn]NiBr ₂ | 0.0483 | 22 | 8660 | 0 | 0.11 | 0.8963 | 130 | 143 | 550 | 3.86 |
| 307 | [(iPr ₂ Ph ₂)DABAn]NiCl ₂ | 0.0283 | 11 | 8740 | 0 | 0 | 0.8957 | 190 | 220 | 808 | 3.68 |
| 308 | [(iPr ₂ Ph ₂)DABMe ₂]NiBr ₂ | 0.0188 | 15 | 10200 | 0 | 0 | 0.8753 | 280 | 632 | 1725 | 2.73 |
| 309 | [(Me ₂ Ph ₂)DABMe ₂]NiBr ₂ | 0.0283 | 11 | 10400 | 0.26 | 16 | 0.9095 | 150 | 38 | 110 | 2.92 |
| 310 | [(Me ₂ Ph ₂)DABH ₂]Ni(acac) ₂ | 0.0085 | 6 | 10600 | ND | ND | ND | 520 | ND | ND | ND |
| 311 | [(Me ₂ Ph ₂)DABH ₂]NiBr ₂ | 0.0312 | 9 | 12600 | 4.4 | 169 | 0.9527 | 130 | 15 | 86 | 5.93 |
| 312 | [(Me ₂ Ph ₂)DABMe ₂]NiCl ₂ | 0.0328 | 5 | 13100 | 0.03 | 5.5 | 0.9107 | 110 | 53 | 164 | 3.10 |
| 313 | [(Me ₂ Ph ₂)DABMe ₂]Ni(acac) ₂ | 0.0313 | 7 | 17000 | ND | ND | ND | 150 | ND | ND | ND |
| 314 | [(iPr ₂ Ph ₂)DABMe ₂]NiCl ₂ | 0.0202 | 7 | 17100 | 0 | 0 | 0.8817 | 220 | 390 | 1228 | 3.15 |
| 315 | [(Me ₂ Ph ₂)DABMe ₂]Ni(acac) ₂ | 0.0158 | 5 | 18400 | 0.02 | 3.0 | 0.9215 | 300 | ND | ND | ND |
| 316 | [(iPr ₂ Ph ₂)DABMe ₂]NiCl ₂ | 0.0185 | 17 | 52100 | 0 | 0 | 0.8805 | 250 | ND | ND | ND |

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| Run # | Catalyst | Mass cat. (g) | Run Time (mins) | Productivity (g PE/g Ni) | MI | HLMI | Density (g/cc) | Al:Ni | Mn | Mw | HI |
|-------|------------------------------------|---------------|-----------------|--------------------------|-----|------|----------------|-------|-----|------|-----|
| 317 | $[(iPr_2Ph_2)DABAn]Ni(hfacac)_2$ | 0.0048 | 16 | 104000 | 0 | 0.08 | 0.9011 | 1700 | 309 | 1366 | 4.4 |
| 318 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0088 | 19 | 116000 | 0 | 0 | 0.8867 | 680 | ND | ND | ND |
| 319 | $[(Me_2Ph_2)DABH_2]Ni(hfacac)_2$ | 0.0034 | 4 | 137000 | 1.3 | 78 | 0.9569 | 1850 | ND | ND | ND |
| 320 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0029 | 14 | 302000 | 0 | 0 | 0.8986 | 2600 | 788 | 2389 | 3.0 |

TABLE 4 (all Runs were at 80°C)

| Run # | Catalyst | Mass cat. (g) | Run Time (mins) | Productivity (g PE/g Ni) | MI | HLMII | Density (g/cc) | Al:Ni | Mn | Mw | HI |
|-------|---|---------------|-----------------|--------------------------|------|-------|----------------|-------|-----|------|------|
| 401 | [(iPr ₂ Ph ₂)DABAn]NiCl ₂ | 0.0326 | 9 | 1980 | ND | ND | 0.9048 | 160 | ND | ND | ND |
| 402 | [(Me ₂ Ph ₂)DABH ₂]Ni(acac) ₂ | 0.0161 | 3 | 3860 | 0.46 | 24 | 0.9246 | 280 | ND | ND | ND |
| 403 | [(iPr ₂ Ph ₂)DABAn]NiBr ₂ | 0.0239 | 5 | 4580 | 0 | 1.5 | 0.8644 | 260 | ND | ND | ND |
| 404 | [(Me ₂ Ph ₂)DABH ₂]NiBr ₂ | 0.0318 | 6 | 5160 | 16 | ND | 0.9466 | 130 | 12 | 44 | 3.62 |
| 405 | [(Me ₂ Ph ₂)DABMe ₂]Ni(acac) ₂ | 0.0253 | 3 | 6650 | 1.5 | 67 | 0.9118 | 180 | ND | ND | ND |
| 406 | [(iPr ₂ Ph ₂)DABMe ₂]NiBr ₂ | 0.0363 | 5 | 6740 | 0 | 0 | 0.8680 | 150 | 255 | 652 | 2.56 |
| 407 | [(Me ₂ Ph ₂)DABMe ₂]Ni(acac) ₂ | 0.0131 | 4 | 7140 | ND | ND | ND | 360 | ND | ND | ND |
| 408 | [(Me ₂ Ph ₂)DABMe ₂]NiBr ₂ | 0.0263 | 9 | 9920 | 72 | ND | ND | 160 | 14 | 31 | 2.22 |
| 409 | [(Me ₂ Ph ₂)DABH ₂]Ni(hfacac) ₂ | 0.0035 | 2 | 10800 | ND | ND | 0.9997 | 1800 | ND | ND | ND |
| 410 | [(iPr ₂ Ph ₂)DABAn]Ni(hfacac) ₂ | 0.0202 | 4 | 24600 | 0 | 0.12 | 0.8899 | 410 | 145 | 644 | 4.4 |
| 411 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(hfacac)Cl | 0.0088 | 4 | 25700 | 0 | 0.04 | 0.8867 | 680 | ND | ND | ND |
| 412 | [(iPr ₂ Ph ₂)DABMe ₂]Ni(hfacac) ₂ | 0.0059 | 4 | 83600 | 0 | 0 | 0.8912 | 1300 | 394 | 1713 | 4.3 |

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The results in Tables 2,3, and 4 show that the high productivity seen with nickel diimine complexes containing one or two β -diketonate or β -ketoester ligands is maintained when temperature (and therefore dissolved ethylene concentration as well) and the diimine ligand are changed. Again, note that reactor temperatures were within commercially acceptable ranges, i.e., between 40 and 80°C.

EXAMPLE 3

This example shows that the high productivity seen with diimine nickel complexes containing one or two β -ketoester ligands is maintained at low Al:Ni ratios; i.e., low levels of MAO. Again, all of the following polymerizations were carried out as described above, with a reactor pressure of 550 psig ethylene in isobutane slurry. MAO was added in a 10% wt/wt solution in toluene. Catalyst system used in Runs 523-527 were physically mixed with an inert, filler material before addition to the reactor in order to expedite weighing small amounts of catalyst system. Then, the actual mass of catalyst system added to the reactor was calculated, based on the weight ratio of filler and catalyst system combined.

TABLE 5

| Run # | Catalyst | Mass cat. (g) | T (°C) | Run Time (mins) | Productivity (g PE/g Ni) | MI | HLMi | Density (g/cc) | Al:Ni |
|-------|---|---------------|--------|-----------------|--------------------------|------|------|----------------|-------|
| 501 | $[(Me_2Ph)_2DABH_2]Ni(acac)_2$ | 0.0110 | 13 | 9 | 87200 | 0 | 0.19 | 0.9348 | 160 |
| 502 | $[(Me_2Ph)_2DABH_2]Ni(acac)_2$ | 0.0362 | 27 | 11 | 29000 | 0 | 0.45 | 0.9305 | 120 |
| 503 | $[(Me_2Ph)_2DABMe_2]Ni(acac)_2$ | 0.0147 | 27 | 17 | 78800 | 0 | 0.33 | 0.9331 | 320 |
| 504 | $[(Me_2Ph)_2DABH_2]Ni(acac)_2$ | 0.0139 | 27 | 10 | 78000 | 0 | 0.15 | 0.9180 | 320 |
| 505 | $[(iPr_2Ph)_2DABMe_2]Ni(hfacac)_2$ | 0.0204 | 27 | 30 | 149000 | 0 | 0 | 0.8951 | 370 |
| 506 | $[(iPr_2Ph)_2DABMe_2]Ni(hfacac)Cl$ | 0.0134 | 27 | 35 | 199000 | 0 | 0 | 0.9002 | 450 |
| 507 | $[(Me_2Ph)_2DABMe_2]Ni(acac)_2$ | 0.0090 | 27 | 14 | 82100 | ND | ND | ND | 520 |
| 508 | $[(Me_2Ph)_2DABH_2]Ni(acac)_2$ | 0.0448 | 40 | 7 | 28500 | 0 | 0.34 | 0.9221 | 100 |
| 509 | $[(Me_2Ph)_2DABH_2]Ni(hfacac)_2$ | 0.0050 | 40 | 5 | 52700 | 1.5 | 51 | 0.9608 | 250 |
| 510 | $[(Me_2Ph)_2DABMe_2]Ni(acac)_2$ | 0.0185 | 40 | 10 | 51800 | 0 | 0.12 | 0.9360 | 250 |
| 511 | $[(iPr_2Ph)_2DABMe_2]Ni(allOacac)_2$ | 0.0209 | 40 | 27 | 21300 | 0 | 0 | 0.9157 | 300 |
| 512 | $[(iPr_2Ph)_2DABMe_2]Ni(PhCF_3acac)_2$ | 0.0165 | 40 | 41 | 33700 | 0 | 0 | 0.9137 | 460 |
| 513 | $[(iPr_2Ph)_2DABMe_2]Ni(CF_3CF_2CF_2tBuacac)_2$ | 0.0608 | 60 | 7 | 4430 | 0 | 0 | <0.8800 | 150 |
| 514 | $[(Me_2Ph)_2DABMe_2]Ni(acac)_2$ | 0.0313 | 60 | 7 | 17000 | ND | ND | ND | 150 |
| 515 | $[(Me_2Ph)_2DABMe_2]Ni(acac)_2$ | 0.0158 | 60 | 5 | 18400 | 0.02 | 3.0 | 0.9215 | 300 |
| 516 | $[(iPr_2Ph)_2DABMe_2]Ni(allOacac)_2$ | 0.0177 | 60 | 4 | 6450 | 0 | 0 | 0.9060 | 360 |
| 517 | $[(Me_2Ph)_2DABMe_2]Ni(acac)_2$ | 0.0253 | 80 | 3 | 6650 | 1.5 | 67 | 0.9118 | 180 |

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| Run # | Catalyst | Mass cat. (g) | T (°C) | Run Time (mins) | Productivity (g PE/g Ni) | MI | HLM | Density (g/cc) | Al:Ni |
|-------|---|---------------|--------|-----------------|--------------------------|------|------|----------------|-------|
| 518 | $[(iPr_2Ph_2)DABMe_2]Ni(CF_3furacac)_2$ | 0.0310 | 80 | 6 | 8600 | 0 | 0.08 | 0.8836 | 240 |
| 519 | $[(Me_2Ph_2)DABH_2]Ni(acac)_2$ | 0.0161 | 80 | 3 | 3900 | 0.46 | 24 | 0.9246 | 280 |
| 520 | $[(iPr_2Ph_2)DABMe_2]Ni(PhCF_3acac)_2$ | 0.0216 | 80 | 4 | 12000 | 0 | 0.04 | 0.9013 | 350 |
| 521 | $[(Me_2Ph_2)DABMe_2]Ni(acac)_2$ | 0.0131 | 80 | 4 | 7140 | ND | ND | ND | 360 |
| 522 | $[(iPr_2Ph_2)DABAn]Ni(hfacac)_2$ | 0.0202 | 80 | 4 | 24600 | 0 | 0.12 | 0.8899 | 410 |
| 523 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0038 | 40 | 16 | 116000 | ND | ND | ND | 1590 |
| 524 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0054 | 40 | 10 | 53000 | ND | ND | ND | 830 |
| 525 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0046 | 40 | 20 | 169000 | ND | ND | ND | 660 |
| 526 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0044 | 40 | 47 | 104000 | ND | ND | ND | 340 |
| 527 | $[(iPr_2Ph_2)DABMe_2]Ni(hfacac)_2$ | 0.0052 | 40 | 28 | 99000 | ND | ND | ND | 140 |

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The data in Table 5 show that high productivity can be achieved with diimine nickel complexes containing one or two β -diketonate or β -ketoester groups with low levels of MAO. Runs 523-527 clearly demonstrate that very high productivities can be achieved even at very low Al:Ni molar ratios, i.e., low amounts of MAO added to the polymerization reaction.

EXAMPLE 4

This Example shows that inventive catalyst systems can be used to produce syndiotactic polymers. The term "syndiotactic polymer", as used herein, includes those polymers having segments of more than 10 monomeric units in which the alkyl groups of each successive monomeric unit is on the opposite side of the plane of the polymer. Syndiotactic polymers produced according to the invention can have a wide range of applications based upon their physical properties. These syndiotactic polymers can be molded by heat to form shaped objects and they can be used to form fibers or filaments. These syndiotactic polymers also can be used for blending with polymers of different tacticity to vary the properties of such polymers.

In this example where information is given about the microstructure of polymers as determined by ^{13}C NMR, spectra were taken using standard accepted spectroscopy techniques. Polymer was dissolved in 1,2,4-trichlorobenzene and the spectra was taken with respect to an internal standard relative to hexamethylsiloxane which has a known reference point relative to tetramethylsilane; the base standard in the NMR spectra was 0 ppm based on tetramethylsilane. From the observed integrals of the relevant peaks, the details regarding the microstructure are calculated.

$$\text{Meso Content} = (\text{mm}) + \frac{1}{2} (\text{mr})$$

$$\text{Racemic Content} = (\text{rr}) + \frac{1}{2} (\text{mr})$$

$$\text{Isotacticity} = \% (\text{mm})$$

$$\text{Heterotacticity} = \% (\text{mr})$$

$$\text{Syndiotacticity} = \% (\text{rr})$$

$$\text{Randomness Index} = \frac{(\text{mr})100}{2(\text{m})(\text{r})}$$

$$\text{Average Isotactic Block Length} = 1 + \frac{2(\text{mm})}{(\text{mr})}$$

$$\text{Average Syndiotactic Block Length} = 1 + \frac{2(\text{rr})}{(\text{mr})}$$

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For more detail regarding the determination of these values, reference can be made to Chapter 3 of Chain Structure and Conformation of Macromolecules (Academic Press, 1982) by Frank A. Bovey.

Polymerization was carried out as described above. Reactor temperature was 80°C. 0.0140 g of N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(II) bis(acetylacetonate), designated as [(iPr₂Ph)₂DABMe₂]Ni(acac)₂ the nickel catalyst system and 5 mls of MAO (10 weight % in toluene) were added to the reactor, followed by propylene. Propylene was fed on demand and the polymerization reaction terminated when propylene flow into the reactor ceased. Hydrogen was not added to the reactor. After one hour of reaction time, isobutane was removed to yield 4.2 g of polymer. Productivity was 2660 g polypropylene/g Ni. Polymer characterization by ¹³CNMR is as follows.

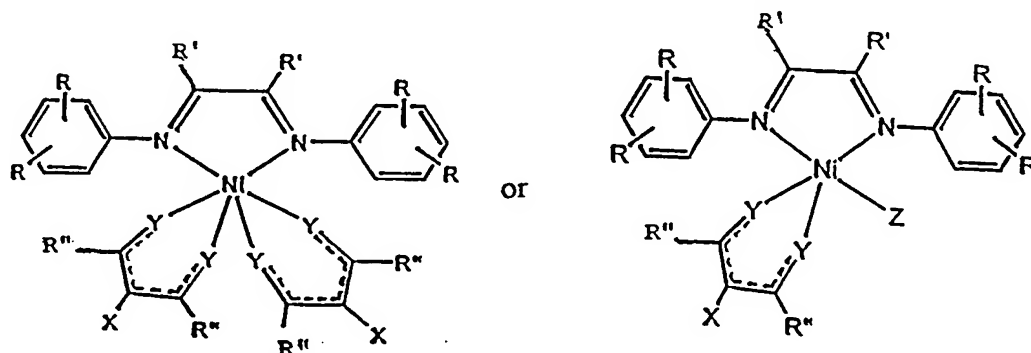
| | |
|---------------|-------------|
| %[mm] = 6.00 | %[m] = 17.1 |
| %[mr] = 22.17 | %[r] = 7.48 |
| %[rr] = 71.83 | |

The above data demonstrates that the inventive catalyst systems can produce syndiotactic polymers, such as syndiotactic polypropylene, as shown by approximately 72% rr triads as determined by ¹³CNMR spectroscopy. While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

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CLAIMS

1. A heterogeneous catalyst composition comprising:
a) a diimine nickel complex having a formula which is



wherein R can be the same or different and is a branched or linear alkyl or aromatic group having from about 1 to about 10 carbon atoms per alkyl group and can be in any position on the aromatic ring;

wherein R' can be the same or different and is hydrogen or a
15 linear, branched, cyclic, bridging, aromatic, and/or aliphatic hydrocarbon having from about 1 to about 70 carbon atoms per radical group;

wherein R''CYCXCYP can be the same or different and is an α -deprotonated- β -diketone, an α -deprotonated- β -ketoester, a halogen or a mixture of any of two or more of said radicals, and wherein R and X can be the same or different and are individually hydrogen or a linear, branched, cyclic,
20 bridging, aromatic or aliphatic hydrocarbon, or a mixture of any two or more of said radicals having from about 1 to about 70 carbon atoms per radical group.

wherein Y can be the same or different and is oxygen, sulfur, or
25 selenium; and

wherein Z is a halogen which is fluorine, chlorine, bromine, or iodine;
and

b) methylaluminoxane.

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2. A composition according to claim 1, wherein said diimine nickel complex and said methylaluminoxane are present in an amount so as to have an aluminum to nickel molar ratio of less than about 850:1.
3. A composition according to claim 1, wherein said aluminum to
5 nickel molar ratio in said catalyst system is within a range of about 50:1 to about 1200:1.
4. A composition according to claim 3, wherein said aluminum to nickel molar ratio is within a range of about 50:1 to about 600:1.
5. A composition according to claim 1, wherein said R substituent is
10 a linear or branched aliphatic group having from about 1 to about 8 carbon atoms per group.
6. A composition according to claim 5, wherein said R substituent is a linear or branched alkyl group having from about 1 to about 8 carbon atoms per group.
- 15 7. A composition according to claim 6, wherein said R substituent is a methyl group, an isopropyl group, or a mixture thereof.
8. A composition according to claim 1, wherein said R' substituent is hydrogen or a branched, linear, cyclic, aromatic or aliphatic hydrocarbon radical or a mixture of any two or more of said radicals having from about 1
20 to about 20 carbon atoms per radical.
9. A composition according to claim 8, wherein said R' substituent is hydrogen or a branched, linear, cyclic, aromatic or aliphatic hydrocarbon radical having from about 1 to about 12 carbon atoms per radical.
10. A composition according to claim 9, wherein said R' substituent
25 is hydrogen, a methyl group, an ethyl group, a propyl group, a phenyl group, an acenaphthyl group, a cyclobutadienyl group or a mixture of any two or more of said groups.
11. A composition according to claim 1, wherein R" and X are
30 individually hydrogen or a hydrocarbon radical having from about 1 to about 10 carbon atoms per radical group.

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12. A composition according to claim 1, wherein one said R" and X are individually hydrogen or a linear, branched, cyclic, bridging, aromatic, or aliphatic hydrocarbon radical, or a mixture of any two or more of said radicals having from about 1 to about 70 carbon atoms per radical group, and wherein
5 another said R" is an alkoxide of a linear, a branched, a cyclic, a bridging, an aromatic, or an aliphatic hydrocarbon radical, or a mixture of any two or more of said radicals having from about 1 to about 70 carbon atoms per radical group.

13. A composition according to claim 12, wherein one said R",
10 another said R" and X each have from about 1 to about 10 carbon atoms per radical group.

14. A process according to claim 1, wherein said R"CYCXCYP" is 2,4-pentanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, allylacetonacetate, benzoyl-acetate, benzoyl-1,1,1-trifluoroacetone, 1,1,1-trifluoro-2,4-pentane-
15 dione, 1-chloro-1,1-difluoroacetylacetone methyl-4,4,4-trifluoroacetoacetate, 1,1,1-trifluoro-5,5-dimethyl-2,4-pentanedione, ethyl alpha-methyl-4,4,4-trifluoroacetoacetate, 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione, or 2,2-dimethyl-6, 6, 7,7,8,8,8-heptafluoro-3,5-octanedione; and

Z is chloride or bromide.

15. A process for polymerizing an olefin which comprises contacting
20 in a reaction zone under slurry polymerization reactor conditions:

a) an olefin monomer; and

b) a heterogenous catalyst composition according to any one of the preceding claims.

16. A process according to claim 15, wherein said slurry
25 polymerization reactor conditions comprise a reaction temperature within a range of about 10° to about 90°C and a pressure within a range of about 100 to about 1000 psia.

17. A process according to claim 15, wherein said slurry
30 polymerization is carried out in the presence of an isobutane diluent.

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18. A process according to claim 15, wherein the olefin monomer is ethylene.
19. A process according to claim 18, which further comprises contacting a comonomer which is an alpha-olefin having from 3 to 10 carbon atoms per molecule with (a) and (b).
20. A process according to claim 19, wherein said comonomer is propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-pentene, or a mixture of any two or more of said comonomers.
21. A process according to claim 20, wherein said comonomer is 1-hexene, 4-methyl-1-pentene, or a mixture thereof.
22. A process according to claim 15, wherein the olefin monomer is propylene.
23. A process according to claim 22, which further comprises contacting a comonomer which is an alpha-olefin having from 2 to 10 carbon atoms per molecule with (a) and (b).
24. A process according to claim 22, which produces a polymer of syndiotactic polypropylene.
25. A polymer composition of ethylene comprising from 20 to 3000 short chain branches per 10,000 backbone carbon atoms of said polymer; and wherein said polymer has a heterogeneity index in the range of about 3 to about 8.
26. A heterogeneous catalyst composition substantially as herein described with reference to any one of the Examples.
27. A process for polymerizing an olefin according to claim 15, substantially as herein described with reference to any one of the Examples.
28. A polymer when produced by a process according to any one of claims 15-24 and 27.
29. A polymer composition of ethylene substantially as herein described with reference to any one of Examples 1-3.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/25889

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : 502/117; 526/172, 348, 348.2, 348.4, 348.5

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/117; 526/172, 348, 348.2, 348.4, 348.5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A. | US 3,592,870 A (DUAN) 13 July 1971, whole document. | 1-29 |
| A | US 3,949,013 A (YOO et al) 06 April 1976, whole document. | 1-29 |
| A | US 5,852,145 A (MCLAIN et al) 22 December 1998, whole document. | 1-29 |
| X,P | US 5,844,055 A (BRANDT et al) 01 December 1998, abstract, col. 8-9, table 3. | 25 |
| Y,P | | 28, 29 |
| X,E | US 5,866,663 A (BROOKHART et al) 02 February 1999, col. 74, examples. | 25 |
| Y,E | | 28, 29 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

| | |
|---|--|
| * Special categories of cited documents: | *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| *A* document defining the general state of the art which is not considered to be of particular relevance | *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| *B* earlier document published on or after the international filing date | *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | *G* document member of the same patent family |
| *O* document referring to an oral disclosure, use, exhibition or other means | |
| *P* document published prior to the international filing date but later than the priority date claimed | |

Date of the actual completion of the international search

16 MARCH 1999

Date of mailing of the international search report

15 APR 1999

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/25889

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☒

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/25889

A. CLASSIFICATION OF SUBJECT MATTER: IPC (6):

B01J 31/00, 37/00; C08F 4/02, 4/60, 4/06, 210/00, 10/14, 110/14, 210/14

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-24, 26 and 27, drawn to a two component catalyst composition and method of polymerizing olefins using the same.

Group II, claim(s) 25, 28 and 29, drawn to polyolefins.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the polymers of group II do not require the use of the special technical feature of the catalysts or method of polymerization of group I to make them. The polymers are conventional.

